Xanthen-9-ylidene protecting groups in glycerol chemistry

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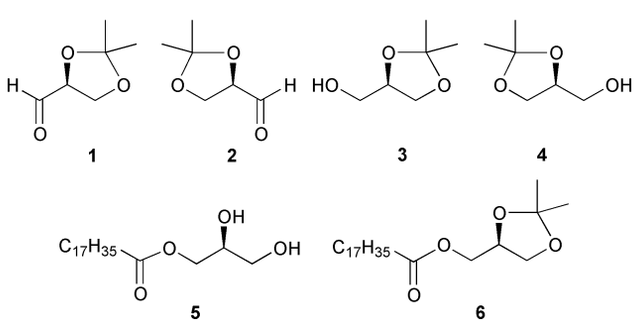
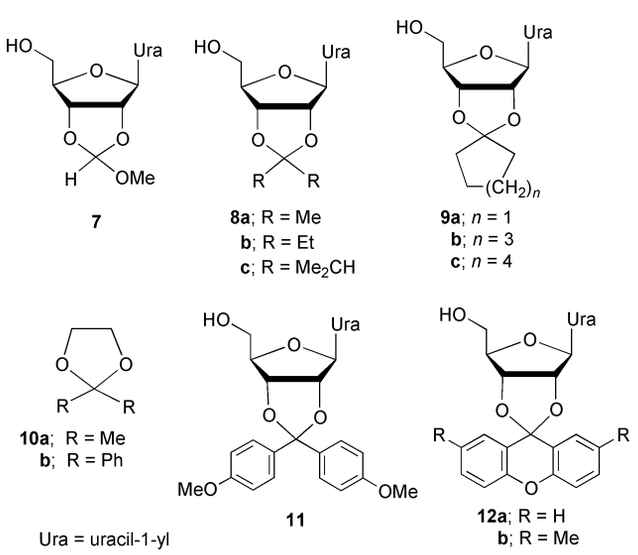
The preparation of racemic, (*S*)- and (*R*)-1,2-*O*-(xanthen-9-ylidene)glycerol **17a**, **20a** and **23a** and racemic, (*S*)- and (*R*)-1,2-*O*-(2,7-dimethylxanthen-9-ylidene)glycerol **17b**, **20b** and **23b** is reported. The racemic derivatives **17a** and **17b** are converted into their stearate esters, which are then treated with dichloroacetic acid and pyrrole under mild conditions to give racemic 1-*O*-stearoylglycerol **25** in good yield. The xanthen-9-ylidene and 2,7-dimethylxanthen-9-ylidene residues are incorporated into 9,9-di(pyrrol-2-yl)xanthene **36** and 2,7-dimethyl-9,9-di(pyrrol-2-yl)xanthene **37**. These by-products are easily removed by treatment with iron(III) chloride in diethyl ether solution. What are believed to be enantiomerically pure (*R*)- and (*S*)-1-*O*-stearoylglycerol **28** and **5** are similarly prepared in good yields from (*S*)- and (*R*)-1,2-*O*-(xanthen-9-ylidene)glycerol **20a** and **23a**.

Introduction

(*S*)- and (*R*)-2,3-*O*-Isopropylideneglyceraldehyde **1** and **2** are valuable chiral building blocks that are both relatively easy to prepare[1,2] in high enantiomeric excess. This is also true of (*R*)- and (*S*)-1,2-*O*-isopropylideneglycerol **3** and **4** which may readily be obtained[3] by the sodium borohydride reduction of the corresponding glyceraldehyde derivatives **1** and **2**. Recently, in connection with our work on the synthesis of phosphatidylinositol 3,4,5-trisphosphate[4,5] [PtdIns(3,4,5)P_3], we needed to prepare (*S*)-1-*O*-stearoylglycerol **5**. The acidic conditions required[5,6] for the unblocking of its precursor isopropylidene derivative **6** were relatively drastic and hence the possibility of acyl migration occurring to a small extent (probably not more than 1%) and consequent racemization could not be ruled out. We therefore decided to undertake the preparation of chiral building blocks corresponding to the isopropylidene derivatives **3** and **4**, but involving an achiral acetal protecting group that was more labile to acidic hydrolysis than the isopropylidene group.



In the 1960s, in connection with our studies on the synthesis of oligoribonucleotides, we found that the methoxymethylene protecting group[7], as in 2′,3′-*O*-(methoxymethylene)uridine **7**, was some two orders of magnitude more labile to acidic hydrolysis than the isopropylidene group in the corresponding uridine derivative **8a**. However, the methoxymethylene group is chiral and its use in glycerol chemistry would lead to undesirable mixtures of diastereoisomers. Shortly afterwards, Hampton *et al.*[8] reported that 2′,3′-*O*-cyclopentylidene-, -cycloheptylidene- and -cyclooctylidene-uridine (**9a**, **9b** and **9c**, respectively) undergo hydrolysis in 0.01 mol dm^{-3} hydrochloric acid at 26 °C *ca.* 5, 7 and 8 times more rapidly than does 2′,3′-*O*-isopropylideneuridine **8a**. On the other hand, 2′,3′-*O*-(pentan-3-ylidene)-[8] and 2′,3′-*O*-(2,4-dimethylpentan-3-ylidene)-[9] uridine (**8b** and **8c**, respectively) have been found to be *ca.* 2 and 7 times *more stable* to acidic hydrolysis than is 2′,3′-*O*-isopropylideneuridine **8a**. Presumably the intermediate oxonium ions (or carbocations) involved in the hydrolysis of compounds **8b** and **8c** are destabilized by steric hindrance. It is likely that there is a similar explanation for the fact[10] that 2,2-diphenyl-1,3-dioxolane **10b** is considerably more stable to acidic hydrolysis than is 2,2-dimethyl-1,3-dioxolane **10a**. However, the lability of the diphenylmethylene protecting group can easily be increased by the introduction of electron-donating aromatic substituents. Thus we have very recently shown[11] that 2′,3′-*O*-[di(*p*-anisyl)-methylene]uridine† **11** is more than twice as labile as is 2′,3′-*O*-isopropylideneuridine **8a** in trifluoroacetic acid–water–methanol (1 : 2 : 7 v/v) solution at 30 °C. We have further shown[11] that, under the same conditions of acidic hydrolysis, 2′,3′-*O*-(xanthen-9-ylidene)- and 2′,3′-*O*-(2,7-dimethylxanthen-9-ylidene)-uridine (**12a** and **12b**, respectively) are *ca.* 5 and 20 times more labile than is 2′,3′-*O*-isopropylideneuridine **8a**. We now report the preparation of both racemic and optically active 1,2-*O*-(xanthen-9-ylidene) and 1,2-*O*-(2,7-dimethylxanthen-9-ylidene) derivatives of glycerol.



† In this paper, *p*-anisyl is used for *p*-methoxyphenyl.

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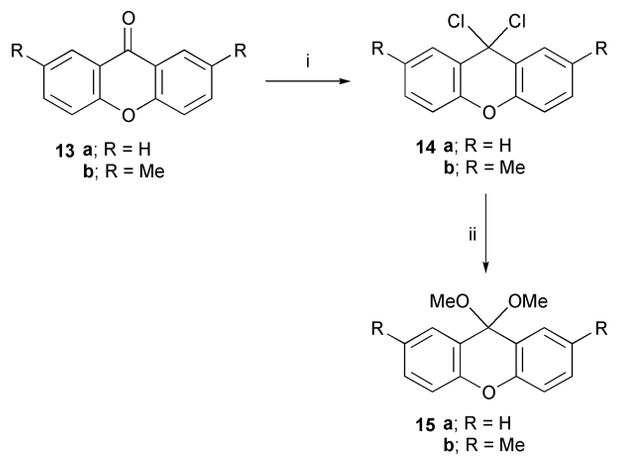
Results and discussion

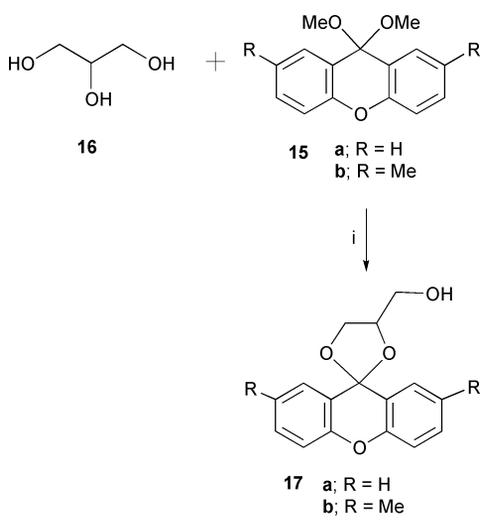
The key reagents required for the preparation of 1,2-*O*-(xanthen-9-ylidene) and 1,2-*O*-(2,7-dimethylxanthen-9-ylidene) derivatives are the 9,9-dichloroxanthenes **14a**,**b** and the corresponding 9,9-dimethoxyxanthenes **15a**,**b**. Following a literature procedure,[12] 9,9-dichloroxanthene **14a** was prepared (Scheme 1, step i) in virtually quantitative yield by heating commercially available xanthen-9-one **13a** with thionyl dichloride, under reflux, in the presence of a catalytic amount of DMF. Treatment of 9,9-dichloroxanthene **14a** with sodium methoxide in methanol–THF (Scheme 1, step ii) gave 9,9-dimethoxy-



Scheme 1 *Reagents and conditions*: i, $SOCl_2$, DMF, reflux; ii, NaOMe, MeOH, THF, 0 °C to room temp.

xanthene[11] **15a** in 94.5% overall yield for the two steps. In the same way, 9,9-dichloro-2,7-dimethylxanthene **14b** and 9,9-dimethoxy-2,7-dimethylxanthene **15b** were prepared[11] from 2,7-dimethylxanthen-9-one **13b** in virtually quantitative and 91% overall yield, respectively. 2,7-Dimethylxanthen-9-one **13b** itself was prepared from commercially available di(*p*-tolyl) ether by a literature procedure[13] and was obtained in 90% isolated yield (Experimental section).

When glycerol **16** was allowed to react with 9,9-dimethoxyxanthene **15a** in the presence of a catalytic quantity of (±)-camphor-10-sulfonic acid (CSA) in acetonitrile solution at room temperature (Scheme 2), racemic 1,2-*O*-(xanthen-9-



Scheme 2 *Reagents and conditions*: i, CSA, MeCN, room temp., 4h.

ylidene)glycerol **17a** was obtained and isolated as a crystalline solid in 81% yield. In the same way, racemic 1,2-*O*-(2,7-dimethylxanthen-9-ylidene)glycerol **17b** was prepared (Scheme 2) and isolated as a crystalline solid in 67% yield. The yield has not been optimized in either of these preparations. Apart from the fact that the xanthen-9-ylidene and 2,7-dimethylxanthen-9-ylidene groups are both more labile to acidic hydrolysis than is the isopropylidene protecting group,[11] these new protected glycerol derivatives **17a** and **17b** have two distinct advantages over 1,2-*O*-isopropylideneglycerol. First, they are both crystalline, and secondly, they both absorb strongly in the ultraviolet (Experimental section).

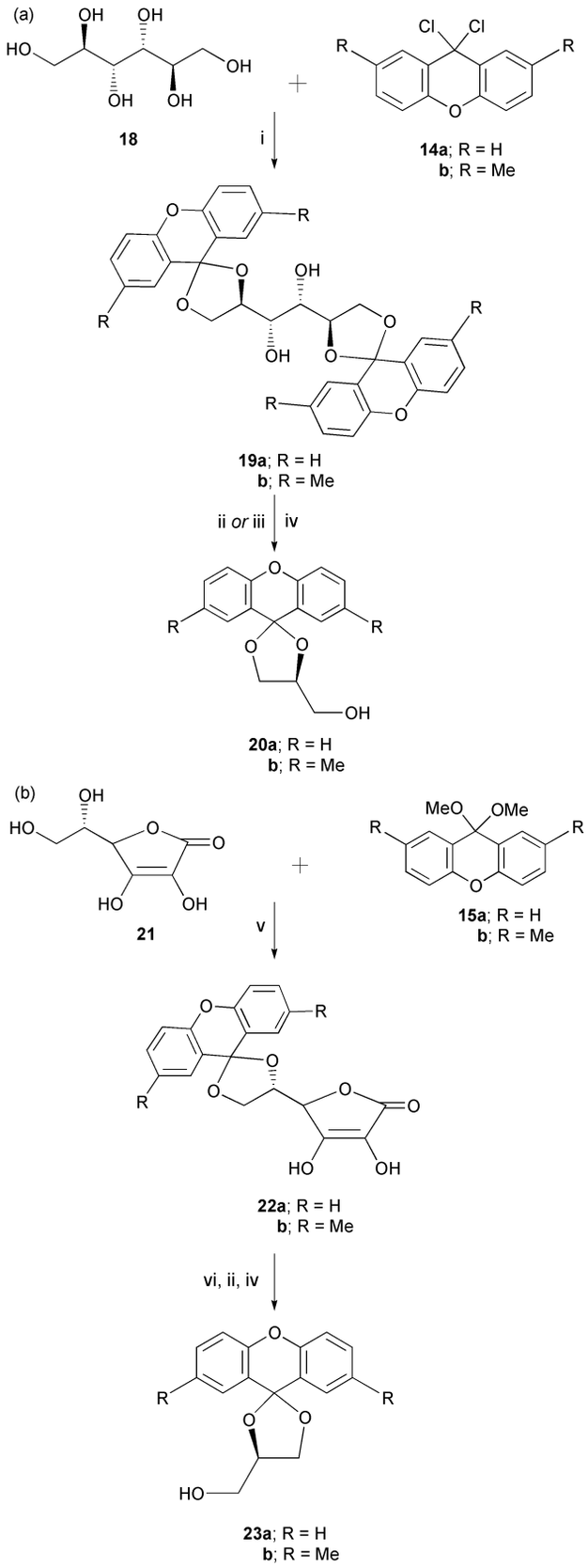
Table 1 Specific rotations of glycerol derivatives

Entry	Compound	$[a]_D^{20}$/deg cm^2 g^{-1}	*c*(ethanol)/g 100 cm^{-3}
1	**20a**	+15.7	1.5
2	**20b**	+18.2	1.5
3	**23a**	−15.3	1.5
4	**23b**	−18.2	1.5

Like (*S*)-1,2-*O*-isopropylideneglycerol[14] **4**, (*S*)-1,2-*O*-(xanthen-9-ylidene)glycerol **20a** and (*S*)-1,2-*O*-(2,7-dimethylxanthen-9-ylidene)glycerol **20b** may both be prepared from D-mannitol **18**. Treatment of D-mannitol with 9,9-dichloroxanthene **14a** in pyridine solution (Scheme 3a) gave 1,2:5,6-di-*O*-(xanthen-9-ylidene)-D-mannitol **19a**, which was isolated as a crystalline solid in 84.5% yield. In the same way, D-mannitol **18** reacted with 9,9-dichloro-2,7-dimethylxanthene **14b** to give its 1,2:5,6-bis-*O*-(2,7-dimethylxanthen-9-ylidene) derivative **19b** in 81% isolated yield. Oxidative cleavage of 1,2:5,6-di-*O*-(xanthen-9-ylidene)-D-mannitol **19a** was effected either with lead(IV) acetate[14] in ethyl acetate or with sodium metaperiodate[2] in aq. THF. In both cases, the putative intermediate glyceraldehyde derivative was reduced with sodium borohydride (Scheme 3a, step iv) to give (*S*)-(+)-(xanthen-9-ylidene)glycerol **20a** as a crystalline solid in 81 and 94% isolated yield, respectively, based on the D-mannitol derivative **19a**. 1,2:5,6-Bis-*O*-(2,7-dimethylxanthen-9-ylidene)-D-mannitol **19b** was similarly treated with sodium metaperiodate and the putative intermediate aldehyde was reduced with sodium borohydride to give (*S*)-(2,7-dimethylxanthen-9-ylidene)glycerol **20b**, which was isolated as a crystalline solid in 69% yield for the two steps. As indicated in Table 1 (entries nos. 1 and 2, respectively), compounds **20a** and **20b** are both dextrorotatory.

Like (*R*)-1,2-*O*-isopropylideneglycerol[15] **3**, (*R*)-1,2-*O*-(xanthen-9-ylidene)glycerol **23a** and (*R*)-1,2-*O*-(2,7-dimethylxanthen-9-ylidene)glycerol **23b** may both be prepared (Scheme 3b) from L-ascorbic acid **21**. Thus L-ascorbic acid was first heated, under reflux, with a slight excess of 9,9-dimethoxyxanthene **15a** in the presence of a catalytic quantity of CSA in dry acetonitrile (Scheme 3b, step v) to give its 5,6-*O*-(xanthen-9-ylidene) derivative **22a**. Following the addition of an excess of lithium carbonate, the products were treated first with aqueous hydrogen peroxide and then with lead(IV) acetate (steps vi and ii, respectively) to give the putative (*S*)-2,3-*O*-(xanthen-9-ylidene)glyceraldehyde. Reduction with sodium borohydride (step iv) gave (*R*)-1,2-*O*-(xanthen-9-ylidene)-glycerol **23a**, which was isolated as a crystalline solid in 41.5% overall yield. In the same way, (*R*)-1,2-*O*-(dimethylxanthen-9-ylidene)glycerol **23b** was prepared from L-ascorbic acid **21** by the same four-step process *via* intermediate **22b**, and was isolated as a crystalline solid in 32% overall yield. Compounds **23a** and **23b** are both laevorotatory (Table 1, entries nos. 3 and 4, respectively) and their specific rotations are very nearly equal and opposite to those of their respective enantiomers (entries nos. 1 and 2).

Racemic 1,2-*O*-(xanthen-9-ylidene)- and 1,2-*O*-(2,7-dimethylxanthen-9-ylidene)-glycerol **17a** and **17b** were both examined as potential starting materials for the preparation of racemic 1-*O*-stearoylglycerol **25**. Treatment of the xanthen-9-ylidene derivative **17a** with stearoyl chloride and 1-methylimidazole in dichloromethane solution (Scheme 4a) gave the putative stearate ester **24a** as the sole product. It was found that the xanthen-9-ylidene protecting group could be removed under very mild



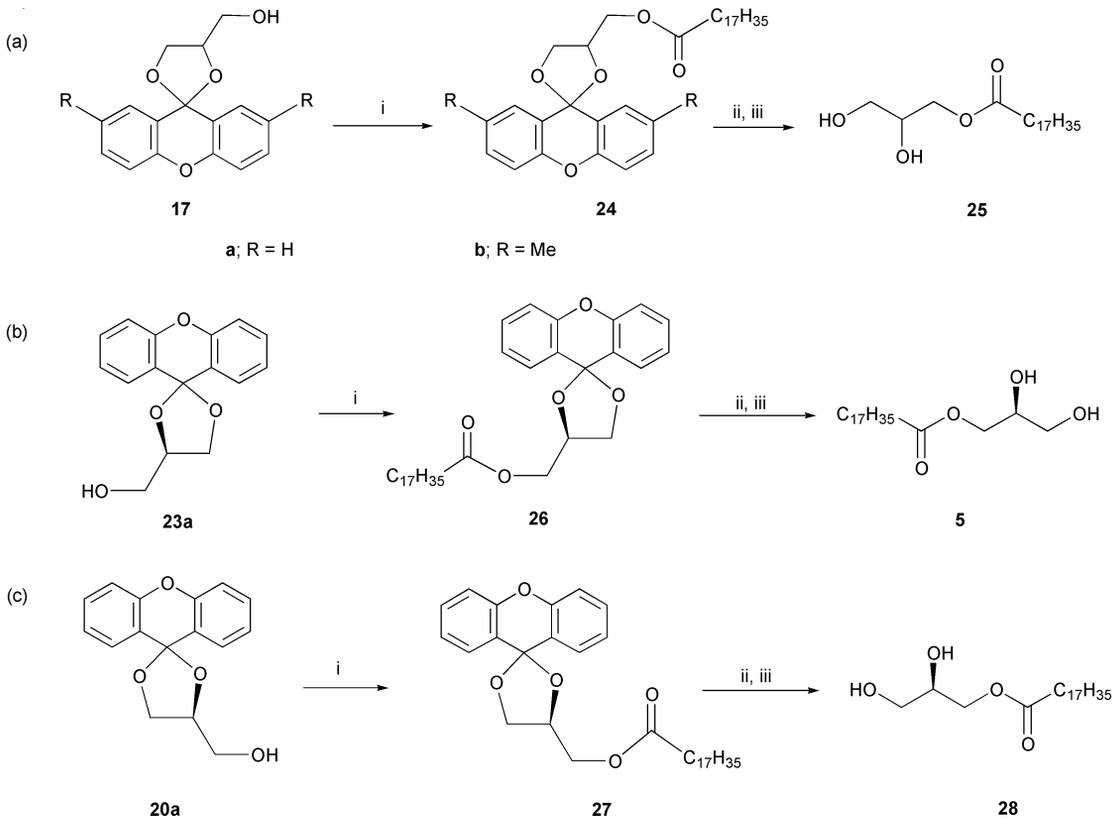
Scheme 3 *Reagents and conditions*: i, C_5H_5N, 0 °C to room temp.; ii, $Pb(OAc)_4$, $NaHCO_3$, EtOAc, room temp.; iii, $NaIO_4$, $NaHCO_3$, aq. THF, room temp., 4 h; iv, $NaBH_4$, EtOH; v, CSA, MeCN, reflux, 3 h; vi, (a) Li_2CO_3; (b) aq. H_2O_2, 0 °C to room temp., 16 h.

conditions indeed. When a *ca.* 0.15 mol dm^{-3} solution of the intermediate stearate ester **24a** in dichloromethane was treated with dichloroacetic acid (*ca.* 4 mol equiv.) and pyrrole[16] (*ca.* 5 mol equiv.) at room temperature, rapid unblocking occurred and, following work-up of the products after 15 min, racemic 1-*O*-stearoylglycerol **25** was isolated as a pure crystalline solid in 80% overall yield. The other product was identified as 9,9-di(pyrrol-2-yl)xanthene **36** (see below and Experimental section). It seemed desirable that the lipid product **25**, which would be expected to undergo acyl migration under mildly basic conditions, should be isolated without recourse to column chromatography. This was achieved by treating a solution of the products (*i.e.*, compounds **25** and **36**) with an excess of iron(III) chloride in diethyl ether solution. In this way, the xanthene derivative **36** was quantitatively removed (see below) and a dark brown solid precipitate was obtained. Following the same procedure (Scheme 4a), racemic 1,2-*O*-(2,7-dimethylxanthen-9-ylidene)glycerol **17b** was also converted into racemic 1-*O*-stearoylglycerol **25**, which was isolated in 85% overall yield. The xanthene by-product **37** (see below) was again removed by the iron(III) chloride precipitation method.

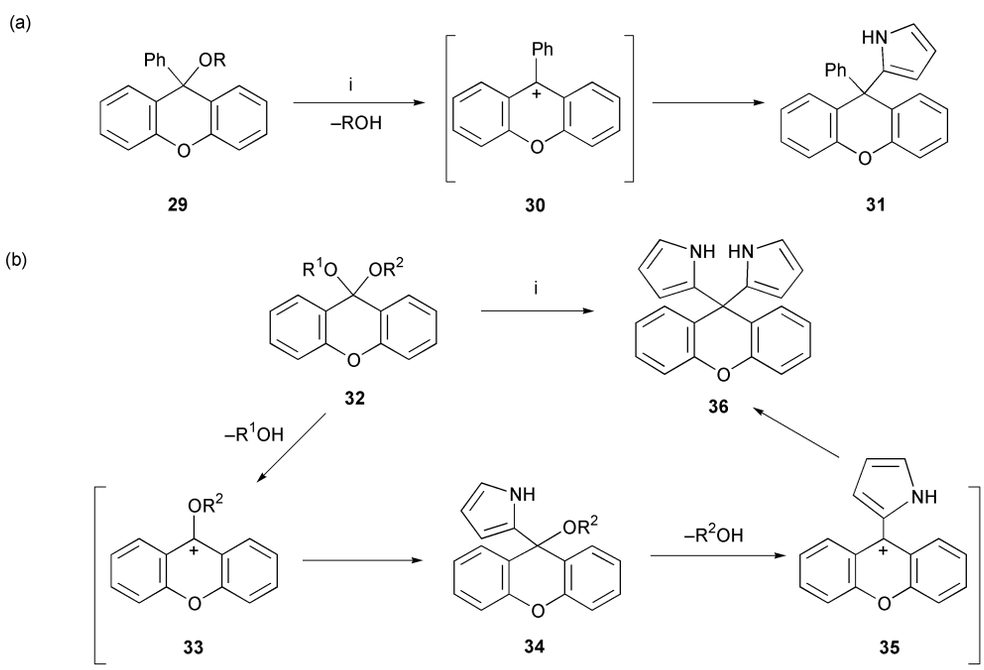
It is noteworthy that the 2,7-dimethylxanthen-9-ylidene derivative **24b** did not appear to undergo more rapid dichloroacetic acid–pyrrole promoted unblocking than the simple xanthen-9-ylidene derivative **24a**. Therefore, if unblocking is to be effected in this way, there appears to be no obvious advantage in using the 2,7-dimethylxanthen-9-ylidene rather than the more easily accessible unsubstituted xanthen-9-ylidene protecting group. For this reason, the enantiomeric (*S*)- and (*R*)-1-*O*-stearoylglycerols **5** and **28** were prepared from the corresponding (*R*)- and (*S*)-1,2-*O*-(xanthen-9-ylidene)glycerol **23a** and **20a** (Schemes 4b and 4c, respectively) by exactly the same procedure as was used for the preparation of the racemic material **25** (Scheme 4a). (*R*)-(−)-1-*O*-Stearoylglycerol **28** {$[a]_D^{20}$ −3.68 (*c* 4.1, C_5H_5N)} and (*S*)-(+)-1-*O*-stearoylglycerol **5** {$[a]_D^{20}$ +3.64 (*c* 4.1, C_5H_5N)} were thereby prepared and isolated in 77 and 79% overall yield, respectively. It appears from the specific rotation data that the present approach to the preparation of (*R*)- and (*S*)-1-*O*-stearoylglycerol **5** and **28** leads to material of even greater enantiomeric purity than was obtained previously.[5,6]

The procedure for the dichloroacetic acid–pyrrole-promoted removal of the xanthen-9-ylidene protecting group is essentially the same as the procedure that we recommended[16] some 15 years ago for the removal of the 9-phenylxanthen-9-yl[17] and related (*e.g.*, 4,4′-dimethoxytrityl[18]) protecting groups from alcoholic hydroxy functions. Thus, when a 9-phenylxanthen-9-yl ether **29** (Scheme 5a) is treated with dichloroacetic acid and pyrrole, the 9-phenylxanthen-9-yl cation **30** is generated and then rapidly and irreversibly quenched by pyrrole to give 2-(9-phenylxanthen-9-yl)pyrrole[16] **31**. The suggested mechanism for the removal of the xanthen-9-ylidene protecting group, which is illustrated in Scheme 5b for an acyclic acetal **32**, is somewhat more complicated. The cation **33** generated initially would perhaps be expected to be as stable as the 9-phenylxanthen-9-yl cation inasmuch as the mesomeric effect of an alkoxy group (OR^2) is generally unlikely to be smaller than that of a phenyl group. The monopyrrol-2-yl intermediate **34**, formed by the reaction between cation **33** and pyrrole, would be expected to fragment very rapidly indeed under the reaction conditions to give cation **35**. This intermediate **35**, which is stabilized by the mesomeric effect of the pyrrol-2-yl residue, would be expected to be more stable than the 9-phenylxanthen-9-yl cation **30**. Although we have not so far obtained any supporting experimental evidence, the inductive effect of the methyl substituents in the 2,7-dimethylxanthen-9-ylidene protecting group (as in **17b**) would be expected to facilitate the transformations indicated in Scheme 5.

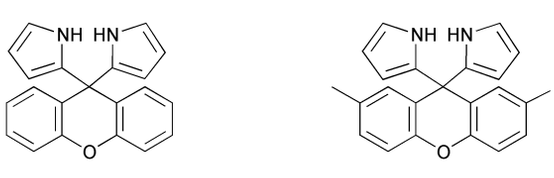
The two di(pyrrol-2-yl) derivatives **36** and **37** were both obtained as pure crystalline compounds and were fully characterized. Racemic 1-*O*-stearoyl-2,3-*O*-(xanthen-9-ylidene)-glycerol **24a** was treated with an excess each of dichloroacetic acid and pyrrole in dichloromethane solution at room temperature. Following fractionation of the products, the di(pyrrol-2-yl) derivative **36** was isolated as a colourless crystalline solid in



Scheme 4 *Reagents and conditions*: i, $CH_3(CH_2)_{16}COCl$, 1-methylimidazole, CH_2Cl_2, room temp., 90 min; ii, (a) pyrrole, $Cl_2CHCOOH$, CH_2Cl_2, room temp., 15 min; (b) $FeCl_3$, Et_2O, room temp.



Scheme 5 *Reagents*: i, pyrrole, Cl_2CHCO_2H, CH_2Cl_2.



92% yield. The latter compound was also prepared from 9,9-dimethoxyxanthene **15a** and obtained in 74% isolated yield. In the same way, 2,7-dimethyl-9,9-di(pyrrol-2-yl)xanthene **37** was prepared both from racemic 1,2-*O*-(2,7-dimethylxanthen-9-ylidene)-3-*O*-stearoylglycerol **24b** and 9,9-dimethoxy-2,7-dimethylxanthene **15b** and isolated in 82 and 64% yield, respectively. When solutions of each of these di(pyrrol-2-yl) derivatives **36** and **37** were treated with a threefold excess of iron(III) chloride in dry diethyl ether solution, dark coloured solid precipitates were obtained and, in both cases, none of the starting material remained in the ethereal solution. No attempt has so far been made to characterize these precipitated solids.

In conclusion, we believe that (*R*)- and (*S*)-*O*-(xanthen-9-ylidene)glycerol (**23a** and **20a**, respectively) have several distinct advantages as building blocks for the preparation of chiral glycerol derivatives over the corresponding commercially available isopropylidene compounds (**3** and **4**, respectively).

Not only are they crystalline and ultraviolet-absorbing but, following the required transformation or transformations, the xanthen-9-ylidene protecting group can be removed under very mild conditions indeed.

Experimental

Mps were measured with a Büchi melting point apparatus and are uncorrected. ^{1}H NMR spectra were measured at 360 and 400 MHz with Bruker AM 360 and Avance 400 spectrometers. ^{13}C NMR spectra were measured at 90.6 and 100.6 MHz, respectively, with the same spectrometers. Chemical shifts are given in ppm relative to tetramethylsilane, and *J*-values are given in Hz. UV absorption spectra were measured with a Perkin-Elmer Lambda spectrometer. Optical rotations were measured with a Perkin-Elmer 343 polarimeter, and $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Merck silica gel 60 F_{254} plates (Art 5715 and 5642), which were developed in solvent systems A [dichloromethane–methanol (9 : 1 v/v)] and B [petroleum spirit (distillation range 60–80 °C)–ethyl acetate (80 : 20 v/v)] were used for TLC. Merck silica gel 60 (Art 7729 and 9385) were used for short-column chromatography. Acetonitrile and pyridine were dried by heating, under reflux, over calcium hydride and were then distilled; toluene was dried by heating, under reflux, over sodium wire and was then distilled; THF was dried by heating, under reflux, over potassium benzophenone and was then distilled; dichloromethane was dried by heating, under reflux, over phosphorus pentaoxide and was then distilled; methanol was dried by heating, under reflux, over magnesium methoxide (generated *in situ* from magnesium turnings and methanol) and was then distilled. Hereafter, the term petroleum spirit refers to the fraction with distillation range 40–60 °C, unless stated otherwise.

9,9-Dimethoxyxanthene 15a

Xanthen-9-one **13a** (19.6 g, 0.10 mol), DMF (0.5 cm^3) and thionyl dichloride (40 cm^3) were heated together, under reflux, for 4 h. The remaining thionyl dichloride was removed by distillation at atmospheric pressure, followed by evaporation under reduced pressure. The residue was co-evaporated with toluene (4 × 40 cm^3) and then heated at 60 °C *in vacuo* for 1 h to give a pale yellow solid (25.50 g), which was assumed to be 9,9-dichloroxanthene[12] **14a**.

A solution of this material (25.50 g) in dry THF (100 cm^3) was added dropwise over a period of 30 min and in an atmosphere of nitrogen to a cooled (ice–water-bath), stirred solution of methanolic sodium methoxide (*ca.* 4.3 mol dm^{-3}; 76.3 cm^3, *ca.* 0.33 mol). The reactants were allowed to warm to room temperature and, after a further period of 1 h, the products were evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (150 cm^3) and the resulting mixture was washed with saturated aq. sodium hydrogen carbonate (3 × 100 cm^3). The dried ($MgSO_4$) organic layer was evaporated under reduced pressure to give the *title compound* **15a** as a pale yellow solid (22.9 g, 94.5%) [Found, in material recrystallized from ethanol–triethylamine (99 : 1 v/v): C, 74.2; H, 5.6. $C_{15}H_{14}O_3$ requires C, 74.36; H, 5.82%], mp 59–61 °C; δ_H ($CDCl_3$) 2.94 (6 H, s), 7.23 (4 H, m), 7.42 (2 H, m), 7.74 (2 H, m); δ_C ($CDCl_3$) 51.81, 96.60, 116.57, 118.77, 123.38, 127.36, 130.20, 153.23.

2,7-Dimethylxanthen-9-one 13b

Oxalyl dichloride (8.60 cm^3, 98.6 mmol), followed by well powdered aluminium chloride (5.0 g, 37.5 mmol), was added to a cooled (ice–water-bath), stirred solution of di(*p*-tolyl) ether (5.00 g, 25.2 mmol) in carbon disulfide (37 cm^3). After 2 h, more aluminium chloride (4.0 g, 30.0 mmol) was added and the reactants were allowed to warm to room temperature. After 16 h, the products were added slowly to cooled (ice–water–bath), stirred hydrochloric acid (*ca.* 3.2 mol dm^{-3}; 120 cm^3). After 30 min, the organic layer was separated and the aqueous layer was extracted with dichloromethane (5 × 50 cm^3). The combined organic layers were dried ($MgSO_4$), and evaporated under reduced pressure. The residue was stirred with saturated aq. sodium hydrogen carbonate (100 cm^3) at 60 °C for 20 min. The precipitated solid was collected by filtration and recrystallized from absolute ethanol to give 2,7-dimethylxanthen-9-one **13b** (5.10 g, 90%), mp 139–141 °C (lit.,[13] 143 °C); δ_H ($CDCl_3$) 2.45 (6 H, s), 7.35 (2 H, d, *J* 8.5), 7.49 (2 H, dd, *J* 2.2 and 8.7), 8.1 (2 H, d, *J* 1.3); δ_C ($CDCl_3$) 20.78, 117.66, 121.37, 125.95, 133.40, 135.85, 154.36, 177.30.

9,9-Dimethoxy-2,7-dimethylxanthene 15b

2,7-Dimethylxanthen-9-one **13b** (5.00 g, 22.3 mmol), DMF (*ca.* 0.2 cm^3) and thionyl dichloride (25 cm^3) were heated together, under reflux, for 4 h. The products were evaporated to dryness under reduced pressure and the residue was co-evaporated with dry toluene (2 × 15 cm^3) to give a pink solid (6.10 g), which was assumed to be 9,9-dichloro-2,7-dimethylxanthene **14b**.

A solution of this material (6.10 g) in dry THF (50 cm^3) was added dropwise over a period of 30 min and in an atmosphere of nitrogen to a cooled (ice–water-bath), stirred solution of methanolic sodium methoxide (*ca.* 4.3 mol dm^{-3}; 25 cm^3, *ca.* 0.11 mol). The reactants were allowed to warm to room temperature and, after a further period of 1 h, the products were concentrated to dryness under reduced pressure. The residue was dissolved in dichloromethane (100 cm^3) and the solution was washed with saturated aq. sodium hydrogen carbonate (3 × 100 cm^3). The combined aqueous washings were back-extracted with dichloromethane (2 × 100 cm^3). The combined organic layers were dried ($MgSO_4$), and evaporated under reduced pressure to give the *title compound* **15b** (5.50 g, 91%) as a yellow solid [Found, in material recrystallized from ethanol–triethylamine (99 : 1 v/v): C, 75.5; H, 6.7. $C_{17}H_{18}O_3$ requires C, 75.53; H, 6.71%], mp 81–82 °C, δ_H ($CDCl_3$) 2.40 (6 H, s), 2.92 (6 H, s), 7.08 (2 H, d, *J* 8.3), 7.21 (2 H, d, *J* 8.3), 7.50 (2 H, s); δ_C ($CDCl_3$) 20.91, 51.84, 96.94, 116.19, 118.16, 126.98, 131.09, 132.64, 151.45.

(±)-1,2-*O*-(Xanthen-9-ylidene)glycerol 17a

A solution of glycerol **16** (0.74 cm^3, 10.1 mmol) and 9,9-dimethoxyxanthene **15a** (1.21 g, 5.00 mmol) in dry acetonitrile (10 cm^3) was evaporated under reduced pressure. A solution of the residue and (±)-camphor-10-sulfonic acid (0.010 g) in dry acetonitrile (20 cm^3) was stirred in an atmosphere of argon at room temperature. After 4 h, triethylamine (0.1 cm^3) was added and the products were evaporated under reduced pressure. A solution of the residue in dichloromethane (20 cm^3) was washed with saturated aq. sodium hydrogen carbonate (2 × 10 cm^3). The dried ($MgSO_4$) organic layer was concentrated under reduced pressure and the residue was fractionated by short-column chromatography on silica gel: the appropriate fractions, which were eluted with dichloromethane–methanol (99 : 1 v/v), were combined, and evaporated under reduced pressure to give the *title compound* **17a** [Found, in material recrystallized from ethyl acetate–petroleum spirit: C, 70.8; H, 5.2. $C_{16}H_{14}O_4$ requires C, 71.10, H, 5.22%] as a colourless solid (1.10 g, 81%), mp 94–96 °C; R_f 0.52 (system A); λ_{max} (EtOH)/nm 288 (ε/dm^3 mol^{-1} cm^{-1} 3680); δ_H [$(CD_3)_2SO$] 3.74 (2 H, m), 4.06 (1 H, t, *J* 7.9), 4.38 (1 H, dd, *J* 6.3 and 7.9), 4.62 (1 H, m), 5.15 (1 H, t, *J* 5.6), 7.29 (4 H, m), 7.48 (2 H, m), 7.72 (1 H, dd, *J* 1.3 and 7.8), 7.89 (1 H, dd, *J* 1.3 and 7.8); δ_C [$(CD_3)_2SO$] 61.07, 67.37, 78.49, 100.24, 116.17, 116.44, 123.23, 123.48, 123.85, 126.46, 127.02, 130.05, 130.22, 150.65, 151.15.

(±)-1,2-*O*-(2,7-Dimethylxanthen-9-ylidene)glycerol 17b

Glycerol **16** (0.37 cm^3, 5.1 mmol), 9,9-dimethoxy-2,7-dimethylxanthene **15b** (0.81 g, 3.0 mmol) and (±)-camphor-10-sulfonic

acid (0.010 g) were allowed to react together in acetonitrile (20 cm^3) solution as in the above preparation of (±)-1,2-*O*-(xanthen-9-ylidene)glycerol **17a**. The products were worked up and chromatographed in the same way to give the *title compound* **17b** (Found: C, 71.6; H, 6.2. $C_{18}H_{18}O_4 \cdot 0.2\ H_2O$ requires C, 71.60: H, 6.14%) as a colourless solid (0.60 g, 67%), mp 137–138 °C, R_f 0.60 (system A); λ_{max} (EtOH)/nm 297 (ε/$dm^3\ mol^{-1}\ cm^{-1}$ 3910); δ_H [$(CD_3)_2SO$] 2.34 (3 H, s), 2.36 (3 H, s), 3.73 (2 H, m), 4.04 (1 H, t, *J* 7.9), 4.39 (1 H, dd, *J* 6.3 and 7.8), 4.60 (1 H, m), 5.11 (1 H, t, *J* 5.6), 7.15 (2 H, dd, *J* 5.3 and 8.4), 7.24 (2 H, dd, *J* 1.9 and 8.3), 7.48 (1 H, d, *J* 1.4), 7.63 (1 H, d, *J* 1.6); δ_C [$(CD_3)_2SO$] 20.46, 20.50, 61.06, 67.47, 78.27, 100.46, 115.84, 116.09, 122.72, 123.37, 126.18, 126.72, 130.58, 130.76, 132.13, 132.23, 148.70, 149.21.

1,2:5,6-Di-*O*-(xanthen-9-ylidene)-D-mannitol 19a

A solution of D-mannitol **18** (1.82 g, 10.0 mmol) in dry pyridine was evaporated under reduced pressure and the residue was redissolved in dry pyridine (30 cm^3). 9,9-Dichloroxanthene **14a** (see above under preparation of 9,9-dimethoxyxanthene **15a**; 6.32 g, *ca.* 25 mmol) was added to the stirred, cooled (ice–water-bath) solution and the reactants were allowed to warm to room temperature. After 1 h, the products were poured into saturated aq. sodium hydrogen carbonate (150 cm^3). After the resulting mixture had been stirred at room temperature for 1 h, the precipitate was collected by filtration and washed with water (340 cm^3). The air-dried solid was suspended in ethyl acetate (25 cm^3) for 10 min and then petroleum spirit (25 cm^3) was added. After 1 h, the mixture was filtered and the residue was washed with ethyl acetate–petroleum spirit (1:1 v/v; 40 cm^3) to give the *title compound* **19a** as an off-white solid (4.55 g, 84.5%) (Found, in material recrystallized from ethyl acetate: C, 71.0; H, 4.8. $C_{32}H_{26}O_8$ requires C, 70.89: H, 4.91%), mp 222.5–224 °C; R_f 0.53 (system A); δ_H [$(CD_3)_2SO$] 3.83 (2 H, t, *J* 7.7), 4.13 (2 H, m), 4.31 (2 H, dd, *J* 6.2 and 8.3), 4.62 (2 H, dd, *J* 6.9 and 13.9), 5.25 (2 H, d, *J* 7.7), 6.81 (2 H, m), 7.22 (6 H, m), 7.34 (2 H, m), 7.41 (2 H, m), 7.64 (4 H, dd, *J* 1.3 and 7.8); δ_C [$(CD_3)_2SO$] 68.60, 70.91, 77.24, 100.64, 116.56, 116.79, 123.40, 123.73, 123.80, 124.02, 126.79, 127.04, 130.43, 130.51, 150.97, 151.52.

1,2:5,6-Bis-*O*-(2,7-dimethylxanthen-9-ylidene)-D-mannitol 19b

A solution of D-mannitol **18** (0.364 g, 2.0 mmol) in dry pyridine (5 cm^3) was evaporated under reduced pressure. The residue was re-evaporated with dry pyridine (5 cm^3) and was then suspended in dry pyridine (10 cm^3). 9,9-Dichloro-2,7-dimethylxanthene **14b** (see above under preparation of 9,9-dimethoxy-2,7-dimethylxanthene **15b**; 1.34 g, *ca.* 4.8 mmol) was added to the cooled (ice–water-bath), stirred solution. After 10 min, the reactants were allowed to warm to room temperature with continued stirring. After a further period of 2 h, methanol (1 cm^3) was added and the products were concentrated under reduced pressure. The residue was partitioned between dichloromethane (50 cm^3) and saturated aq. sodium hydrogen carbonate (50 cm^3). The dried ($MgSO_4$) organic layer was evaporated under reduced pressure. The residue was purified by short column chromatography on silica gel; the appropriate fractions, which were eluted with dichloromethane–methanol (99 : 1 v/v), were combined, and evaporated under reduced pressure to give the *title compound* **19b** as a colourless froth (0.97 g, 81%) (Found: M^+, 594.2231. $^{12}C_{36}{}^{1}H_{34}{}^{16}O_8$ requires *M*, 594.2254), R_f 0.59 (system A); δ_H ($CDCl_3$) 2.00 (6 H, s), 2.37 (6 H, s), 3.93 (2 H, d, *J* 7.7), 4.19 (2 H, t, *J* 7.8), 4.40 (2 H, m), 4.72 (2 H, m), 5.36 (2 H, d, *J* 7.7), 7.15 (6 H, m), 7.26 (2 H, m), 7.47 (4 H, d, *J* 6.9); δ_C ($CDCl_3$) 20.00, 20.44, 68.16, 70.61, 76.93, 100.51, 115.80, 116.07, 122.52, 123.21, 126.43, 130.57, 130.64, 132.13, 148.66, 149.13.

(*S*)-(+)-1,2-*O*-(Xanthen-9-ylidene)glycerol 20a

(a) Lead(IV) acetate (9.05 g, 20.4 mmol) was added in one portion to a stirred, cooled (ice–water-bath) mixture of 1,2:5,6-di-*O*-(xanthen-9-ylidene)-D-mannitol **19a** (3.15 g, 5.85 mmol), sodium hydrogen carbonate (1.96 g, 23.3 mmol) and ethyl acetate (115 cm^3). After 1 h, the products were filtered through a bed of Celite (20 g) and the residue was washed with ethyl acetate (30 cm^3). The combined filtrate and washings were added dropwise over a period of 15 min to a stirred solution of sodium borohydride (1.75 g, 46.3 mmol) in ethanol (115 cm^3) at 0 °C (ice–water-bath). After a further period of 1 h, sodium hydroxide pellets (0.80 g) and then 1.0 mol dm^{-3} aq. sodium hydroxide (50 cm^3) were added with continued stirring. The products were filtered and the layers were separated. The aqueous layer was extracted with dichloromethane (3 × 20 cm^3) and the combined organic layers were concentrated to dryness (water-pump, followed by oil-pump). When petroleum spirit (100 cm^3) was added to a solution of the residue in dichloromethane (20 cm^3), the *title compound* **20a** (2.58 g, 81%) [Found, in material recrystallized from ethyl acetate–petroleum spirit: C, 70.85; H, 5.1. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%] was obtained as a colourless solid, mp 105–107 °C; R_f 0.52 (system A); $[a]_D^{20}$ +15.7 (*c* 1.5, ethanol). The ^1H and ^{13}C NMR spectra [$(CD_3)_2SO$] were identical with those indicated above for the racemic material.

(b) Water (1.0 cm^3), sodium hydrogen carbonate (0.10 g, 1.2 mmol) and sodium metaperiodate (0.853 g, 4.0 mmol) were added to a stirred solution of 1,2:5,6-di-*O*-(xanthen-9-ylidene)-D-mannitol **19a** (0.538 g, 1.00 mmol) in THF (10 cm^3) at room temperature. After 4 h, the products were concentrated under reduced pressure. The residue was dissolved in dichloromethane (30 cm^3) and the solution was washed with saturated aq. sodium hydrogen carbonate (2 × 30 cm^3). The combined aq. layers were back-extracted with dichloromethane (2 × 20 cm^3). The combined organic layers were dried ($MgSO_4$) and then added dropwise over a period of 15 min to a stirred solution of sodium borohydride (0.227 g, 6.0 mmol) in absolute ethanol (10 cm^3) at room temperature. After a further period of 1 h, acetone (5 cm^3) was added and 10 min later the products were concentrated to dryness under reduced pressure. The residue was dissolved in dichloromethane (20 cm^3) and the solution was washed with saturated aq. sodium hydrogen carbonate (3 × 20 cm^3) The combined aq. layers were back-extracted with dichloromethane (2 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), and evaporated under reduced pressure to give a colourless residue, which was crystallized from ethyl acetate–petroleum spirit to give the *title compound* **20a** (0.508 g, 94%) as a colourless solid. This material was identical in all respects with that described under heading (a) above.

(*S*)-(+)-1,2-*O*-(2,7-Dimethylxanthen-9-ylidene)glycerol 20b

Water (1.5 cm^3), sodium hydrogen carbonate (0.05 g, 0.6 mmol) and sodium metaperiodate (0.236 g, 1.1 mmol) were added to a stirred solution of 1,2:5,6-bis-*O*-(2,7-dimethylxanthen-9-ylidene)-D-mannitol **19b** (0.330 g, 0.55 mmol) in THF (5 cm^3) at room temperature. After 3 h, the products were concentrated under reduced pressure and the residue was partitioned between dichloromethane (15 cm^3) and saturated aq. sodium hydrogen carbonate (15 cm^3). The aqueous layer was separated and back-extracted with dichloromethane (2 × 5 cm^3). The combined organic layers were dried ($MgSO_4$) and added dropwise over a period of 30 min to a suspension of sodium borohydride (0.083 g, 2.2 mmol) in ethanol (5 cm^3). After 30 min, acetone (1 cm^3) was added. After a further period of 10 min, the products were evaporated under reduced pressure. The residue was partitioned between dichloromethane (15 cm^3) and saturated aq. sodium hydrogen carbonate (15 cm^3). The layers were separated and the aqueous layer was back-extracted with dichloromethane (2 × 5 cm^3). The combined organic layers were dried ($MgSO_4$), and concentrated under reduced pressure. The residue was fractionated by short-column chromatography

on silica gel: the appropriate fractions, which were eluted with dichloromethane–methanol (99 : 1 v/v), were combined, and evaporated under reduced pressure to give the *title compound* **20b** as a colourless glass (0.230 g, 69%), which later solidified [Found, in material recrystallized from ethyl acetate–petroleum spirit: C, 72.2; H, 6.0. $C_{18}H_{18}O_4$ requires C, 72.47; H, 6.08%], mp 143–144 °C; R_f 0.60 (system A); $[\alpha]_D^{20}$ +18.2 (*c* 1.5, ethanol). The ^{1}H and ^{13}C NMR spectra [$(CD_3)_2SO$] were identical with the corresponding spectra obtained from the racemic material **17b** (see above).

(*R*)-(−)-2,3-*O*-(Xanthen-9-ylidene)glycerol 23a

A solution of L-ascorbic acid **21** (2.67 g, 15.2 mmol) and 9,9-dimethoxyxanthene **15a** (4.5 g, 18.6 mmol) in dry acetonitrile (20 cm^3) was evaporated under reduced pressure. The residue was redissolved in dry acetonitrile (40 cm^3) and (±)-camphor-10-sulfonic acid (0.05 g, 0.22 mmol) was added. The reactants were heated, under reflux, in an atmosphere of nitrogen for 3 h. The cooled products were concentrated to half volume and lithium carbonate (2.29 g, 31 mmol) was added. The resulting mixture was evaporated to dryness under reduced pressure and the residue was dissolved in water (70 cm^3). Aq. hydrogen peroxide (*ca.* 27%; 5.5 cm^3, *ca.* 48 mmol) was added dropwise over a period of 5 min to the stirred, cooled (ice–water-bath) solution. After a further period of 10 min, the reactants were allowed to warm up to room temperature. After 16 h, the products were filtered and the filtrate was concentrated to dryness under reduced pressure. After it had been co-evaporated with absolute ethanol (220 cm^3), the residue was extracted with boiling ethanol (270 cm^3). The extract was concentrated to dryness under reduced pressure (water-pump, followed by oil-pump). The residue was dissolved in ethyl acetate (60 cm^3) and sodium hydrogen carbonate (2.56 g, 30.5 mmol) was added. Lead(IV) acetate (6.80 g, 15.2 mmol) was then added in two portions to the cooled (ice–water-bath), stirred mixture. After 30 min, the reactants were allowed to warm up to room temperature. After a further period of 3 h, the products were cooled (ice–water-bath), and filtered through a bed of Celite. The residue was washed with ice-cold ethyl acetate (40 cm^3). The combined filtrate and washings were added dropwise over a period of 20 min to a cooled (ice–water-bath), stirred suspension of sodium borohydride (0.756 g, 20 mmol) in absolute ethanol (80 cm^3) The reactants were then allowed to warm up to room temperature. After a further period of 3 h, aq. sodium hydroxide (1.0 mol dm^{-3}; 40 cm^3) was added to the products and stirring was continued for an additional 30 min. The layers were separated and the aq. layer was extracted with dichloromethane (4 × 60 cm^3). The combined organic layers were concentrated under reduced pressure and the residue was partitioned between dichloromethane (50 cm^3) and water (50 cm^3). The aqueous layer was back-extracted with dichloromethane (3 × 75 cm^3). The combined organic layers were dried ($MgSO_4$), and evaporated under reduced pressure. The residue was fractionated by short-column chromatography on silica gel: the appropriate fractions, which were eluted with dichloromethane, were combined, and evaporated under reduced pressure to give the *title compound* **23a** as a colourless solid (1.70 g, 41.5% overall yield) [Found, in material recrystallized from ethyl acetate–petroleum spirit: C, 70.7; H, 5.3. $C_{16}H_{14}O_4 \cdot 0.1H_2O$ requires C, 70.63; H, 5.26%], mp 105–106 °C; R_f 0.52 (system A); $[\alpha]_D^{20}$ −15.3 (*c* 1.5, ethanol). The ^{1}H and ^{13}C NMR spectra of this compound were identical with the corresponding spectra of the racemic material **17a** (see above).

R-(−)-2,3-*O*-(2,7-Dimethylxanthen-9-ylidene)glycerol 23b

L-Ascorbic acid **21** (1.48 g, 8.4 mmol) was heated, under reflux, with 9,9-dimethoxy-2,7-dimethylxanthene **15b** (2.7 g, 10.0 mmol) in the presence of (±)-camphor-10-sulfonic acid (0.02 g, 0.09 mmol) in dry acetonitrile (30 cm^3) for 3 h as in the above preparation of (*R*)-(−)-2,3-*O*-(xanthen-9-ylidene)glycerol **23a**. Subsequent reactions with aq. hydrogen peroxide, lead(IV) acetate in ethyl acetate, and sodium borohydride in ethanol–ethyl acetate, as in the above preparation of (*R*)-(−)-2,3-*O*-(xanthen-9-ylidene)glycerol **23a** and with the same stoichiometry gave, after chromatography, the *title compound* **23b** as a colourless solid (0.800 g, 32% overall yield) [Found, in material recrystallized from ethyl acetate–petroleum spirit: C, 72.4; H, 6.1. $C_{18}H_{18}O_4$ requires C, 72.47; H, 6.08%], mp 143–144 °C; R_f 0.60 (system A); $[\alpha]_D^{20}$ −18.2 (*c* 1.5, ethanol). The ^{1}H and ^{13}C NMR spectra of this compound were identical with the corresponding spectra of the racemic material **17b** (see above).

(±)-1-*O*-Stearoylglycerol 25

(a) A solution of stearoyl chloride (1.09 g, 3.6 mmol) in dichloromethane (15 cm^3) was added to a stirred solution of (±)-1,2-*O*-(xanthen-9-ylidene)glycerol **17a** (0.811 g, 3.0 mmol) and 1-methylimidazole (0.477 cm^3, 6.0 mmol) in dichloromethane (15 cm^3) at room temperature. After 90 min, triethylamine (1.0 cm^3) and water (0.2 cm^3) were added. The resulting solution was stirred for 10 min and was then poured into saturated aq. sodium hydrogen carbonate (15 cm^3). The layers were separated and the dried ($MgSO_4$) organic layer was evaporated under reduced pressure. A solution of the residue in methanol (15 cm^3) was stirred at room temperature for 30 min and was then cooled (ice–water-bath) to give putative (±)-1-*O*-stearoyl-2,3-*O*-(xanthen-9-ylidene)glycerol **24a** as a colourless solid precipitate (1.432 g), which was collected by filtration.

This material (0.532 g, *ca.* 1.0 mmol) was dissolved in pyrrole–dichloromethane (1 : 9 v/v; 3.4 cm^3, *ca.* 4.9 mmol of pyrrole), and dichloroacetic acid–dichloromethane (1 : 9 v/v; 3.4 cm^3, *ca.* 4.1 mmol of dichloroacetic acid) was added to the stirred solution at room temperature. After 15 min, dichloromethane (10 cm^3) was added and the products were extracted with 1.0 mol dm^{-3} aq. sodium phosphate buffer (pH 6.0; 20 cm^3). The layers were separated and the organic layer was washed with the same phosphate buffer (15 cm^3). The combined aqueous layers were back-extracted with dichloromethane (20 cm^3). The combined organic layers were dried ($MgSO_4$), and concentrated under reduced pressure. The residue was dissolved in diethyl ether (20 cm^3) and a solution of anhydrous iron(III) chloride (0.487 g, 3.0 mmol) in diethyl ether (30 cm^3) was added to the stirred solution at room temperature. After 30 min, the products were filtered and the residue was washed with diethyl ether (2 × 15 cm^3). The combined filtrate and washings were extracted with the above phosphate buffer (4 × 25 cm^3). The combined aqueous extracts were filtered through a bed of Celite and were then back-extracted with diethyl ether (2 × 15 cm^3). The combined ether layers were dried ($MgSO_4$), concentrated to *ca.* 50 cm^3, and then stirred with activated charcoal (0.3 g) for 30 min. The mixture was then filtered through a bed of Celite and the residue was washed with diethyl ether (2 × 15 cm^3). Evaporation of the filtrate and washings gave the *title compound* **25** (0.320 g, 80%) (Found, in material recrystallized from hexane: C, 69.5; H, 11.75. $C_{21}H_{42}O_4 \cdot 0.25\ H_2O$ requires C, 69.47; H, 11.80%) as a colourless solid, mp 72–73 °C; δ_H ($CDCl_3$) 0.81 (3 H, t, *J* 6.8), 1.20 (28 H, m), 1.55 (2 H, m), 2.28 (2 H, t, *J* 7.6), 3.53 (1 H, dd, *J* 5.8 and 11.5), 3.63 (1 H, dd, *J* 3.9 and 11.5), 3.87 (1 H, m), 4.08 (1 H, dd, *J* 6.1 and 11.7), 4.14 (1 H, dd, *J* 4,7 and 11.7); δ_C [$(CD_3)_2SO$] 13.88, 22.06, 24.39, 28.43, 28.68, 28.86, 29.00, 30.33, 31.26, 33.41, 62.56, 65.41, 69.21, 172.85.

(b) The above experiment was repeated on the same scale and with the same stoichiometry, but starting from (±)-1,2-*O*-(2,7-dimethylxanthen-9-ylidene)glycerol **17b** (0.895 g, 3.0 mmol) instead of (±)-1,2-*O*-(xanthen-9-ylidene)glycerol **17a**. The intermediate putative 1,2-*O*-(2,7-dimethylxanthen-9-ylidene)-3-*O*-stearoylglycerol **24b** (1.61 g) was obtained as a colourless solid. This material (0.565 g) was converted into (±)-1-*O*-stearoylglycerol **25** (0.322 g, 85% overall yield) under precisely

the same conditions described under (a) above. The physical properties (mp, ^{1}H and ^{13}C NMR spectra) of this material were identical with those obtained under (a) above, starting from (±)-1,2-*O*-(xanthen-9-ylidene)glycerol **17a**.

(*S*)-(+)-1-*O*-Stearoylglycerol 5

The experiment described under heading (a) above, for compound **25** was repeated on the same scale and with the same stoichiometry, starting from (*R*)-(−)-1,2-*O*-(xanthen-9-ylidene)glycerol **23a** (0.811 g, 3.0 mmol). The intermediate putative (*S*)-1-*O*-stearoyl-2,3-*O*-(xanthen-9-ylidene)glycerol **26** (1.484 g) was obtained as a colourless solid.

This material (0.565 g) was converted into (*S*)-(+)-1-*O*-stearoylglycerol **5** (0.325 g, 79% overall yield) (Found, in material recrystallized from hexane: C, 69.9; H, 11.9. Calc. for $C_{21}H_{42}O_4 \cdot 0.1H_2O$: C, 69.99; H, 11.8%) under precisely the same conditions described above under heading (a); mp 68.5–69.5 °C; $[\alpha]_D^{20}$ +3.64 (*c* 4.1, C_5H_5N). The ^{1}H and ^{13}C NMR spectra of this material were identical with those described under heading (a) for the racemic modification **25**.

(*R*)-(−)-1-*O*-Stearoylglycerol 28

The experiment described under heading (a) above was repeated on the same scale and with the same stoichiometry, starting from (*S*)-(+)-1,2-*O*-(xanthen-9-ylidene)glycerol **20a** (0.487 g, 1.8 mmol). The intermediate putative (*R*)-1-*O*-stearoyl-2,3-*O*-(xanthen-9-ylidene)glycerol **27** (0.842 g) was obtained as a colourless solid.

This material (0.565 g) was converted into (*R*)-(−)-1-*O*-stearoylglycerol **28** (0.333 g, 77% overall yield) (Found, in material recrystallized from hexane: C, 69.8; H, 11.9. Calc. for $C_{21}H_{42}O_4 \cdot 0.2H_2O$: C, 69.61; H, 11.80%), mp 69–70 °C; $[\alpha]_D^{20}$ −3.68 (*c* 4.1, C_5H_5N). The ^{1}H and ^{13}C NMR spectra of this material were identical with those described above for the racemic modification **25**.

9,9-Di(pyrrol-2-yl)xanthene 36

(a) (±)-1-*O*-Stearoyl-2,3-*O*-(xanthen-9-ylidene)glycerol **24** (0.532 g, 1.0 mmol), the putative intermediate in one of the above preparations of (±)-1-*O*-stearoylglycerol **25**, was dissolved in pyrrole–dichloromethane (1 : 9 v/v; 3.4 cm^3; *ca.* 4.9 mmol of pyrrole), and dichloroacetic acid–dichloromethane (1 : 9 v/v; 3.4 cm^3; *ca.* 4.1 mmol of dichloroacetic acid) was added to the stirred solution at room temperature. After 15 min, the products were partitioned between dichloromethane (15 cm^3) and saturated aq. sodium hydrogen carbonate (15 cm^3). The layers were separated. The organic layer was washed with saturated aq. sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was fractionated by short-column chromatography on silica gel: the appropriate fractions, which were eluted with petroleum spirit (60–80 °C)–ethyl acetate (95 : 5 v/v), were combined, and evaporated under reduced pressure to give the *title compound* **36** as a colourless solid (0.285 g, 92%) (Found, in material recrystallized from aq. methanol: C, 80.3; H, 5.0; N, 8.9. $C_{21}H_{16}N_2O \cdot 0.1H_2O$ requires C, 80.28; H, 5.20; N, 8.92%), mp 189–190 °C; R_f 0.44 (system B); δ_H [$(CD_3)_2SO$] 5.37 (2 H, m), 5.86 (2 H, dd, *J* 2.6 and 5.6), 6.63 (2 H, dd, *J* 2.6 and 4.4), 7.04 (4 H, m), 7.14 (2 H, m), 7.28 (2 H, m), 10.35 (2 H, br s); δ_C [$(CD_3)_2SO$] 44.79, 106.36, 108.82, 116.11, 118.99, 123.33, 127.76, 128.31, 129.70, 135.65, 150.84.

(b) 9,9-Dimethoxyxanthene **15a** (0.484 g, 2.0 mmol) was dissolved in pyrrole–dichloromethane (1 : 9 v/v; 6.7 cm^3, *ca.* 9.7 mmol of pyrrole), and dichloroacetic acid–dichloromethane (1 : 9 v/v; 6.7 cm^3; *ca.* 8.1 mmol of dichloroacetic acid) was added to the stirred solution at room temperature. After 20 min, the products were poured into saturated aq. sodium hydrogen carbonate (15 cm^3). The layers were separated, and the organic layer was washed with saturated aq. sodium hydrogen carbonate (15 cm^3), dried ($MgSO_4$), and then evaporated under reduced pressure. The residue was fractionated by short-column chromatography on silica gel to give a colourless solid (0.462 g, 74%), identical in all respects [mp; R_f (System B), ^{1}H and ^{13}C NMR] with the product **36** obtained above under heading (a).

2,7-Dimethyl-9,9-di(pyrrol-2-yl)xanthene 37

(a) (±)1,2-*O*-(2,7-Dimethylxanthen-9-ylidene)-3-*O*-stearoylglycerol **24b** (0.565 g, 1.0 mmol), the putative intermediate in one of the above preparations of (±)-1-*O*-stearoylglycerol **25**, was treated with pyrrole and dichloroacetic acid in dichloromethane solution in precisely the same way and with the same stoichiometry as indicated above under heading (a) for the preparation of 9,9-di(pyrrol-2-yl)xanthene **36**. Following work-up and short-column chromatography of the products on silica gel, the *title compound* **37** was obtained as a colourless solid (0.280 g, 82%) (Found, in material recrystallized from aq. methanol; C, 80.9; H, 5.7; N, 8.2. $C_{23}H_{20}N_2O$ requires C, 81.15; H, 5.92; N, 8.23%), mp 215–216 °C; R_f 0.50 (system B); δ_H [$(CD_3)_2SO$] 2.19 (6 H, s), 5.36 (2 H, dd, *J* 2.9 and 4.5), 5.85 (2 H, dd, *J* 2.6 and 5.5), 6.63 (2 H, dd, *J* 2.5 and 4.3), 6.80 (2 H, d, *J* 1.7), 6.99 (2 H, d, *J* 8.2), 7.06 (2 H, dd, *J* 1.9 and 8.3), 10.28 (2 H, br s); δ_C [$(CD_3)_2SO$] 20.46, 44.35, 105.87, 108.32, 115.34, 118.42, 126.85, 128.35, 129.27, 131.27, 135.27, 148.51.

(b) 9,9-Dimethoxy-2,7-dimethylxanthene **15b** (0.811 g, 3.0 mmol) was treated with pyrrole and dichloroacetic acid in dichloromethane solution in precisely the same way and with the same stoichiometry as indicated above under heading (b) for the preparation of 9,9-di(pyrrol-2-yl)xanthene **36** from 9,9-dimethoxyxanthene **15a**. Following work-up and short-column chromatography of the products on silica gel, a colourless solid (0.662 g, 64%) was obtained. This material was identical in all respects [mp, R_f (system B), ^{1}H and ^{13}C NMR] with the product **37** obtained above under heading (a).

Action of iron(III) chloride on 9,9-di(pyrrol-2-yl)xanthene 36

A solution of anhydrous iron(III) chloride (0.487 g, 3.0 mmol) in dry diethyl ether (30 cm^3) was added to a stirred solution of 9,9-di(pyrrol-2-yl)xanthene **36** (0.312 g, 1.0 mmol) in dry diethyl ether (10 cm^3) at room temperature. After 20 min, the resulting dark brown solid precipitate was collected by filtration, washed with diethyl ether (3 × 20 cm^3), and dried (yield 0.280 g). No remaining 9,9-di(pyrrol-2-yl)xanthene **36** could be detected (by TLC) in the filtrate and washings.

Action of iron(III) chloride on 2,7-dimethyl-9,9-di(pyrrol-2-yl)-xanthene 37

A solution of anhydrous iron(III) chloride (0.487 g, 3.0 mmol) in dry diethyl ether (30 cm^3) was added to a stirred solution of 2,7-dimethyl-9,9-di(pyrrol-2-yl)xanthene **37** (0.340 g, 1.0 mmol) in dry diethyl ether (10 cm^3) at room temperature. After 20 min, the resulting dark red solid precipitate was collected by filtration, washed with diethyl ether (3 × 20 cm^3), and dried (yield 0.290 g). No 2,7-dimethyl-9,9-di(pyrrol-2-yl)xanthene **37** could be detected in the filtrate and washings.

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